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COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

TELEPHONE CRAWFORD 7071

May 7, 1953
Copy No. 48

[redacted]

Report No. 2-6
(Quarterly Summary)

SUBJECT: [redacted] Oak Nitropolymer Research

CONTRACT: Nonr-397(00)

PERIOD COVERED: February 1, 1953 to April 30, 1953

SUBMITTED BY: John T. Minor

APPROVED BY: Jerome Martin
Director of Research

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COMMERCIAL SOLVENTS CORP. Report No. Q-6

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CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of Contract Nonr-397(00).

COMMERCIAL SOLVENTS CORP. Report No. Q-6

I. SUMMARY

A. This quarterly summary report is the sixth under Contract Nonr-397(00) and covers the period from February 1, 1953 to April 30, 1953. The object of this contract is as follows: "Shall conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the application of processes not now employed in the preparations."

B. The more important results and conclusions of the work reported are presented below.

1. The preparation of 2,2-dinitropropyl acrylate by an ester exchange does not produce a polymerizable material without distillation.

2. A process for the preparation of 2,2-dinitropropyl acrylate from acrylyl chloride and 2,2-dinitropropanol produces the monomer in 76% yield.

3. 2,2-Dinitropropyl acrylate prepared from acrylyl chloride and 2,2-dinitropropanol polymerizes in a bulk process to a high molecular weight polymer that is acetone soluble.

II. TECHNICAL PROGRESS

A. INTRODUCTION

The present program is directed towards the development of a pilot plant process for the production of 2,2-dinitropropyl acrylate and its polymerization. The process under investigation utilizes 2,2-dinitropropanol and acrylyl chloride, catalyzed by anhydrous aluminum chloride, to produce a clean monomer without distillation. The 2,2-dinitropropyl acrylate monomer is polymerized in the bulk at initial temperatures of 40-45°C. and catalyzed by 0.25% methyl amyl ketone peroxide. The lower molecular weight fraction of the resulting polymer is removed by dissolving the total quantity of polymer in acetone, then precipitating the higher molecular weight fraction by pouring the acetone solution into methanol.

B. DINITROPROPYL ACRYLATE (DNPA)

An ester exchange between methyl acrylate and dinitropropanol was run to prepare DNPA using the procedure of Marans and Zelinski[1]. After the product had been washed extensively and after the low boiling fractions had been removed by vacuum, there was obtained in 42% yield a material which nitrogen analysis indicated was 47% DNPA in 2,2-dinitropropanol (DNPOH). The color of the product was dark, indicating a need for distillation before this method could be considered for the preparation of DNPA. The undistilled material would not polymerize.

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1. N. S. Marans and R. P. Zelinski, J. Am. Chem. Soc., 72, 2125 (1950).

The esterification as reported before[1] has been studied further. The process uses acrylyl chloride, DNPOH, and anhydrous aluminum chloride as a catalyst. A solvent is used and in addition to chloroform it has been found that methylene chloride and carbon tetrachloride are suitable. Carbon tetrachloride has the advantage of lower cost, but the disadvantage of lower solubility for DNPOH. In various runs, the yield of dry DNPA based on the acrylyl chloride used was 88, 79, 68, 77, 74, and 69%, or an average of 76%.

The acrylyl chloride as obtained contained cuprous chloride as an inhibitor, and was used without purification or removal of the inhibitor. On thorough washing of the DNPA monomer, the inhibitor is removed and no further inhibition is necessary if the monomer is to be used in a few days, or if the monomer is stored in a cold room.

C. THE POLYMERIZATION OF DNPA

Due to the insoluble polymer formed by emulsion techniques and the low yields of low molecular weight polymer formed in solution, the major emphasis of our study on polymerization has been with the bulk or block technique. The catalyst in all cases was methyl amyl ketone peroxide (MAKP). After the monomer with the catalyst has been held in a closed bottle, flushed with nitrogen, for the required time, the resulting solid polymer is dissolved in a volume (in ml.) of acetone numerically equal to twice the weight of the original monomer in grams. The polymer is precipitated by pouring the acetone solution into twice its volume of methanol or ethanol. The polymer is removed and dried at 50°C. in a vacuum oven. Table 1 tabulates various runs with the polymerization conditions and the relative viscosity of the resulting washed polymers in a two per cent, w/v, solution. A relative viscosity ($\eta_r^{2\%}$) of 3.0 or higher is believed to indicate a polymer of acceptable molecular weight.

1. Commercial Solvents Report No. Q-5, p. 4.

TABLE 1

Sample	MAKP	Conditions	Relative Viscosity ($\frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}}$) at 25°C., 2% soln.
387R	1.0%	25°C., 96 hr.; 45°C., 63 hr.	1.45
387SG	"	" " " "	6.40
392SG	"	" " " "	1.50
392R	"	" " " "	1.51
306RR	"	25°C., 40 hr.; 45°C., 50 hr.; 65°C., 90 hr.	1.86
306R	"	" " " " " "	1.67
306R	0.5%	" " " " " "	1.82
313R	"	48°C., 40 hr.; 40°C., 6 hr.	1.29
313RC	"	48°C., 40 hr.; 90°C., 6 hr.; 75°C., 16 hr.	1.29
316R	0.2%	48°C., 48 hr.; 58°C., 48 hr.	1.98
320R	0.5%	3 weeks in sunlight, R.T.	2.98
320RA	None	" " " " " Very slight polymerization	
321R[a]	0.25%	45°C., 89 hr.	2.69
324R	"	R.T., 16 hr.; 43°C., 72 hr.	1.94
325R	"	" " " "	6.10
327R1	"	42°C., 65 hr.	3.60
327R2	"	" "	4.50
327R4[b]	"	42°C., 40 hr.; 54°C., 24 hr.	19.40
331R[c]	"	40°C., 42 hr.; 50°C., 24 hr.; 65°C., 8 hr.	4.47
332R	"	42°C., 76 hr.	3.76
332SG	"	" "	3.72

a - 133 g. sample polymerized in stainless steel cell, 2 in. long x 2 in. diameter
b - 399 g. " " " " " " 6½ in. " x 2 in. "
c - 409 g. " " " " " " 6½ in. " x 2 in. "

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